

**Hair dy composition**

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Inventor(s): MURAI MICHIKI; IMAMURA TAKASHI; SHIBATA YUTAKA  
Applicant(s): KAO CORP (JP)  
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**Abstract**

A hair dye composition comprising the ingredients (A) and (B): (A) Acid dye 0.01 - 0.2 wt.% (B) Organic solvent 0.5 - 50 wt.%, having a pH of 2.0 - 4.5 and a buffer index of 0.01 - 0.2 gram equivalent/litre is disclosed. The composition is capable of gradually making the white hair unobtrusive by a simple use of applying the composition to the hair with bare hands or fingers, allowing to stand for 120 seconds or less and rinsing.

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**Description****TITLE OF THE INVENTION****HAIR DYE COMPOSITION****BACKGROUND OF THE INVENTION 1) Field of the Invention:**

This invention relates to hair dye compositions, and more particularly to easy-to-handle hair dye compositions which are capable of being applied to the hair by bare hands or fingers without use of gloves etc., and are left on the hair only for a short time before being washed away.

**2) Description of the Conventional Art:**

Hair dye compositions containing acid dyes are widely used at homes and beauty parlours because they give less damages to the hair than other hair dye compositions.

When these hair dye compositions containing acid dyes are applied to the hair, gloves or the like means are the must for protecting the users' hands and fingers from being badly stained. Currently, at beauty parlours, beauticians apply the hair dye compositions to the hair wearing gloves and using combs or the like instrument, while carefully trying to avoid the contact of the composition with the hairline skin area, by applying protecting creams to such hairline area in advance. In order to obtain a good hair dyeing effect, it was also necessary to leave the hair to which the hair dye composition had been applied for 10 to 30 minutes under warming. At homes, similar great attention was required in the use of hair dye compositions containing acid dyes: gloves and combs, and 10 to 30 minutes for dyeing.

Under the above circumstances, various studies have been carried out in an attempt to eliminate the aforementioned disadvantages. One approach proposed is a repeated use, like hair rinses, of hair dye compositions containing a low concentration of acid dyes according to which, the dyeing effect will be gradually apparent as the compositions are used repeatedly. This type of hair dye compositions is advantageous in that stains to the hairline and fingers are neglectable even though the composition is applied to the hair with bare hands or fingers, and a relative short time of about 5 minutes is required after the application of the composition before rinsing.

However, the time of 5 minutes is considered to be still long, in view of the manner of use of hair rinses, and improvement is desired.

## SUMMARY OF THE INVENTION

According to the present invention, there is provided a hair dye composition which gives less stain to the bare skin, and is capable of gradually providing the hair with the dyeing effect in a shorter time of contact with the hair. The composition is especially useful for the grizzled hair because the grey or white hair fibers are gradually made unobtrusive as it is repeatedly used.

Accordingly, an object of the present invention is to provide a hair dye composition comprising the following ingredients (A) and (B):

(A) Acid dye 0.01 - 0.2 wt. %

(B) Organic solvent 0.5 - 50 wt.%, having a pH of 2.0 - 4.5 and a buffer index of 0.01 - 0.2 gram equivalent/litre.

This composition is excellent in that it hardly stains the bare skin of hands and fingers, and is capable of providing the hair with the gradual dyeing effect in less than 120 seconds of contact with the hair at each use.

The above and other objects, features and advantages of the present invention will become apparent from the following description.

## DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The acid dyes, which are ingredient (A) of this invention include nitro dyes, azo dyes, nitroso dyes, triphenylmethane dyes, xanthene dyes, quinoline dyes, anthraquinone dyes and indigoid dyes, and in more detail, reference is made to C.I. Acid Red 27, C.I. Acid Red 51, C.I. Acid Red 18, C.I. Acid Red 92, C.I. Acid Red 94, C.I.

Acid Red 52, C.I. Acid Yellow 23, C.I. Food Yellow 3, C.I.

Food Green 3, C.I. Food Blue 2, C.I. Acid Blue 74, C.I.

Pigment Red 57-1, C.I. Acid Red 33, C.I. Pigment Red 63 (Ca), C.I. Acid Red 87, C.I. Acid Red 92, C.I. Acid Red 94, C.I. Acid Orange 7, C.I. Acid Red 95, C.I. Acid Yellow 73, C.I. Acid Yellow 3, C.I. Acid Green 25, C.I. Solvent

Green 7, C.I. Acid Green 5, C.I. Acid Blue 5, C.I. Acid

Blue 9, C.I. Acid Orange 24, C.I. Acid Violet 9, C.I. Food

Red 6, C.I. Acid Red 26, C.I. Food Red 1, C.I. Acid Red 88, C.I. Acid Orange 20, C.I. Acid Yellow 40, C.I. Acid

Yellow 1, C.I. Acid Yellow 36, C.I. Acid Yellow 11, C.I.

Acid Green 1, C.I. Acid Green 3, C.I. Acid Violet 43, C.I.

Acid Black 1. Among them, preferable acid dyes in view of the dyeing performance are C.I. Acid Yellow 23, C.I.

Solvent Green 7, C.I. Acid Red 27, C.I. Acid Red 18, C.I.

Food Green 3, C.I. Food Blue 2, C.I. Acid Blue 9, C.I.

Acid Yellow 1, C.I. Acid Red 52, C.I. Pigment Red 57-1, C.I. Acid Orange 7, C.I. Acid Black 1, C.I. Acid Green 25,

C.I. Acid Violet 43, and in particular, C.I. Acid Black 1,

C.I. Acid Violet 43, C.I. Acid Orange 7, C.I. Acid Yellow 1 and C.I. Acid Red 52. These acid dyes are used singly or in combination of 2 or more as a mixture.

The above-described acid dyes are incorporated into the hair dye composition of the invention in an amount of 0.01 to 0.2 wt. % (hereinafter simply referred to as %) based on the total composition, and it is preferred that 0.02 to 0.1%, more particularly, 0.03 to 0.08% of the dyes be incorporated from the point of securing the dyeing performance and reduced straining to the skin at the same time. An amount less than 0.01% cannot achieve a sufficient hair dyeing effect in a short time contact, while an amount exceeding 0.2% will stain the skin of hands and fingers significantly and thus not practical.

The organic solvents, which are ingredient (B) of this invention include compounds of formula (1), compounds of formula (2) which are N-alkylpyrrolidone and C1 - C4 alkylene carbonate:

wherein R1 is a hydrogen atom, a lower alkyl group or a group



include aliphatic esters, linear or branched alkyl glyceryl ethers and branched higher alcohols.

The hair dye compositions of this invention are prepared by any known processes, by blending the aforementioned ingredients. The manner of use of the compositions is quite similar to that of ordinary hair rinses. In detail, the hair dye compositions of the invention are received by hands or fingers without use of any instruments, applied to the hair, allowed to stand for 120 seconds or less, followed by rinsing. Repeated use of 5 times to 10 times promises the dyeing effect of not showing white hair fibers. From the aspect of the dyeing effect, the hair dye compositions of the present invention are allowed to stand on the hair fibers for 30 to 120 seconds. Great improvement will not be obtained for longer time of contact than 120 seconds.

Accordingly, the hair dye compositions of this invention are capable of making the white hair fibers gradually unobtrusive by very simple steps of applying the compositions to the hair with bare hands or fingers, leaving for a very short time of 120 seconds or less followed by rinsing.

#### Examples

The present invention will now be explained in more detail by way of examples, but they should not be construed as limiting the invention thereto.

#### Examples 1 to 3:

About 10 g of dry white hair fibers were shampooed, drained (weight of the wet hair fibers after drained: 17 g), uniformly and quickly applied with 3 g of a composition in Table 1, allowed to stand for an indicated period of time at 35°C and rinsed. The hair fibers were dried, shampooed, and similar procedures were repeated before evaluation with respect to the color of the hair fibers and staining of the skin of hands or fingers. The color of the hair fibers which was dyed is indicated by dE. The evaluations were conducted according to the following manner: (1) Color (E): Values L, a and b were measured with a color difference meter (CR 200, product of Minolta Co., Ltd.) for each hair-dyed tress. The color difference AE compared with untreated hair fibers was obtained for the evaluation of color or dyeing performance. Greater the value AE, better the dyeing performance.

#### (2) Staining of the skin of hands and fingers:

Ten members of a professional panel received the compositions with bare hands, then washed their hands with soap. Thereafter the remaining stains were checked according to the following criteria: o : Stains of the hands were removed by double (twice) washing with soap.

X : Stains of the hands were not removed by double (twice) washing with soap.

Table 1

Compara. Compn. Invention Compn.

1	2	3	1	2	3
(1)Ethanol (%)	25.0	25.0	25.0	25.0	25.0
(2)Benzyl alcohol (%)	3.0	3.0	3.0	3.0	5.0
(3)Citric acid (%)	0.5	0.5	3.0	4.0	10.0
(4)C.I. Acid Black 1 (%)	0.007	0.007	0.04	0.007	0.005
(5)C.I. Acid Violet 43 (%)	0.008	0.008	0.04	0.008	0.005
(6)C.I. Acid Orange 7 (%)	0.035	0.035	0.22	0.035	0.025
(7)Hydroxyethyl-cellulose (%)	1.5	1.5	1.5	1.5	1.5
(8)NaOH v=— ~ so Suitable Amount					
(9)Purified water c   Balance					
pH (aqueous 10 wt% solution)	4.0	4.0	4.0	4.0	3.0
Buffer Index	0.003	0.003	0.013	0.017	0.040

(g equivalent/litre)  
 Time after applica- 30 300 30 30 120 120  
 tion before rinsing sec sec sec sec sec sec  
 Dyeing effect(color) 7 11 23 15 18 14  
 after 1st appln.(E)  
 Dyeing effect(color) 13 19 38 22 26 21  
 after 5th appln.(AE)  
 Stains to hands and  
 fingers

Note) The comparative compositions 1 to 3 and Invention compositions 1 to 3 were prepared in such a manner that all the ingredients excepting purified water and NaOH were mixed in their whole amounts, then NaOH and purified water were added thereto so that the determined pHs and buffer indices were obtained.

From the data in Table 1, it is apparent that the hair dye compositions according to the invention exhibit excellent dyeing effect in a short period of contact with the hair fibers, and stains to hands are readily removed with soap.

#### Comparative Example 4

Ten female monitors (about 10% of their front hair was white) in their forties used a hair dye composition in the following manner. Beauticians washed the monitors' hair and applied about 15 g of Comparative Composition 1 in Table 1. The composition was allowed to stand for 30 seconds at 35°C, rinsed and dried with a hair drier.

Similar operations were repeated for 4 times, and conspicuousness of white hair was visually evaluated by the 10 panel members. The results are shown in Table 2.

#### Example 4

Ten female monitors in their forties (about 10% of their front hair was white) used a hair dye composition in the following manner. Beauticians washed the monitors' hair and applied about 15 g of Invention Composition 1 in Table 1. The composition was allowed to stand for 30 seconds at 35°C, rinsed and dried with a hair drier.

Similar operations were repeated for 4 times, and conspicuousness of white hair was visually evaluated by the 10 panel members. The results are shown in Table 2.

#### Example 5

Ten female monitors in their forties used the belowdescribed hair dye composition in the following manner.

About 10% of their front hair was white. Beauticians washed the monitors' hair and applied about 15 g of the composition. The composition was allowed to stand for 90 seconds at 35°C, rinsed and dried with a hair drier.

Similar operations were repeated for 4 times, and conspicuousness of white hair was visually evaluated by the 10 panel members. The results are shown in Table 2. The hand stains of the beauticians after dyeing the hair were removed by washing with soap. The composition was obtained by the similar procedures as described in Examples 1 - 3. The composition had a pH of 4.0 and a buffer index of 0.024 g equivalent/litre.

#### Ingredients Amount (%)

- (1) 1,3-Butanediol 20
- (2) N-methylpyrrolidone 10
- (3) Citric acid 6
- (4) C.I. Acid Black 1 0.006
- (5) C.I. Acid Violet 43 0.003
- (6) C.I. Acid Red 52 0.004
- (7) C.I. Acid Orange 7 0.035
- (8) Xanthan gum 1.0
- (9) NaOH Suitable amount
- (10) Purified water Balance

#### Table 2

No change in Conspicuous- White hair

conspicuous- ness of white are no more  
ness of white hair is some- conspicuous  
hair what mitigated  
Comparative 72 26 2

Comparative 72 26 2

### Composition 4

Invention 17 66 17

### Composition 4

Invention 12 68 20

### Composition 5

Note) The change in the color of the hair of the monitors before and after the use of the composition was observed by panel members, and classified into 3 groups of "No change in conspicuousness of white hair", "Conspicuousness of white hair is somewhat mitigated" and "White hairs are no more conspicuous". Ten panel members evaluated the results of 10 monitors, accordingly, the total number of data is 100.

### Examples 6 to 8

The following compositions exhibited an excellent coloring effect under the conditions of 60 seconds (at 35°C) from the application of the composition to the hair before rinsing and repeated use of about 5 times. The stains on hands were removed by washing with soap. The compositions were prepared in a similar manner as described in Examples 1 to 3. The pH of the compositions was 3.5. The invention compositions 6 and 8 had a buffer index of 0.025 gram equivalent/litre, and the invention composition 7 had a buffer index of 0.037 gram equivalent/litre.

**(Formulation of Invention Composition 6)**

[illegible]

- (1) Ethanol 20
- (2) Benzyl alcohol 5
- (3) Lactic acid 5
- (4) C.I. Acid Black 1 0.004
- (5) C.I. Acid Violet 43 0.005
- (6) C.I. Acid Yellow 1 0.009
- (7) C.I. Acid Orange 7 0.030
- (8) Hydroxyethylcellulose 1.5
- (9) NaOH Suitable amount
- (10) Purified water Balance

(Formulation of Invention Composition 7)

Ingredients	Amount (%)
Water	50.0
Sodium Hydroxide	1.0
Hydrochloric Acid	1.0
Ammonium Hydroxide	1.0
Acetic Acid	1.0
Formic Acid	1.0
Malic Acid	1.0
Succinic Acid	1.0
Tartaric Acid	1.0
Citric Acid	1.0
Ascorbic Acid	1.0
Glucuronic Acid	1.0
Gallic Acid	1.0
Ellagic Acid	1.0
Resorcinol	1.0
Phenol	1.0
Catechol	1.0
Hydroquinone	1.0
Naphthol	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0
Indole	1.0
Pyridine	1.0
Quinoline	1.0
Acridine	1.0
Phenanthrene	1.0
Anthracene	1.0
Fluorene	1.0

- (1) Ethanol 20
- (2) 2-Benzyloxyethanol 5
- (3) Lactic acid 7
- (4) C.I. Acid Black 1 0.005
- (5) C.I. Acid Violet 43 0.005
- (6) C.I. Acid Orange 7 0.045
- (7) Polymer JR-400\*1) 0.3
- (8) Amisoft LS-11\*2) 0.3
- (9) Hydroxyethylcellulose 1.7
- (10) NaOH Suitable amount
- (11) Purified water Balance \*1): Cationized cellulose, product of UCC.

\*2): Monosodium salt of lauroyl glutamate, product of Ajinomoto K.K.

(Formulation of Invention Composition 8)

[illegible]

- (1) 1,3-Butanediol 25  
(2) Benzyl alcohol 5  
(3) Lactic acid 7  
(4) C.I. Acid Black 1 0.015  
(5) C.I. Acid Violet 43 0.030  
(6) C.I. Acid Orange 7 0.020  
(7) Polyether modified silicone\*3) 0.5  
(8) Dimethylpolysiloxane\*4) 0.3  
(9) Xanthan gum 1.0  
(10) NaOH Suitable amount  
(11) Purified water Balance \*3): KF352A, product of Shin-Etsu Chemical Co., Ltd.

**\*4): 4,000,000 cst.**

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## Claims

## Claims

1. A hair dye composition comprising the ingredients (A) and (B):

(A) Acid dye 0.01 - 0.2 wt. %

(B) Organic solvent 0.5 - 50 wt.%, having a pH of 2.0 - 4.5 and a buffer index of 0.01 - 0.2 gram equivalent/litre.

2. The hair dye composition according to Claim 1, wherein the acid dye is selected from the group consisting of C.I. Acid Yellow 23, C.I. Solvent Green 7, C.I. Acid Red 27, C.I. Acid Red 18, C.I. Food Green 3, C.I. Food Blue 2, C.I. Acid Blue 9, C.I. Acid Yellow 1, C.I. Acid Red 52, C.I. Pigment Red 57-1, C.I. Acid Orange 7, C.I.

**Acid Black 1, C.I. Acid Green 25 and C.I. Acid Violet 43.**

3. The hair dye composition according to Claim 1, wherein the acid dye is selected from the group consisting of C.I. Acid Black 1, C.I. Acid Violet 43, C.I. Acid Orange 7, C.I. Acid Yellow 1 and C.I. Acid Red 52.

4. The hair dye composition according to Claim 1, wherein the organic solvent is N-alkylpyrrolidone, C1 - C4 alkylene carbonate or a compound of the following formula (1):

wherein R1 is a hydrogen atom, a lower alkyl group or a group

wherein R2 is a hydrogen atom, a methyl or methoxy group and Rj is a bond or a C1 to C3 saturated or unsaturated divalent hydrocarbon group, Y and Z are independently a hydrogen atom or a hydroxyl group, and p, q and r are independently an integer of 0 to 5 excepting the following two cases (a) and (b):

(a):  $p=q=r=0$  and  $Z=H$ ,  
(b):  $p=q=r=0$ ,  $R1=H$  and  $Z=OH$ .

5. The hair dye composition according to Claim 1, wherein the organic solvent is selected from the group consisting of ethanol, isopropanol, n-propanol, n-butanol, isobutanol, ethylene glycol, propylene glycol, 1,3butanediol, benzyl alcohol, cinnamyl alcohol, phenetyl alcohol, p-anisyl alcohol, p-methylbenzyl alcohol, phenoxy ethanol, 2-benzyloxyethanol, methyl carbitol, ethyl carbitol, propyl carbitol, butyl carbitol, triethylene glycol monoethyl ether, triethylene glycol monobutyl ether, glycerol, N-methylpyrrolidone, N octylpyrrol idone and N-laurylpyrrolidone.

6. The hair dye composition according to Claim 1, wherein the pH of 2.0 - 4.5 and buffer index of 0.01 - 0.2 gram equivalent/litre are obtained by the incorporation of a compound selected from the group consisting of citric acid, glycolic acid, succinic acid, tartaric acid, lactic acid, fumaric acid, malic acid, levulinic acid, butyric acid, valeric acid, oxalic acid, maleic acid and mandelic acid, phosphoric acid, sulfuric acid, nitric acid and salts thereof.

7. A method of use a hair dye composition comprising the ingredients (A) and (B):

(A) Acid dye 0.01 - 0.2 wt. %

(B) Organic solvent 0.5 - 50 wt.%, having a pH of 2.0 - 4.5 and a buffer index of 0.01 - 0.2 gram equivalent/litre, which comprises applying the composition to the hair with bare hands or fingers, allowing to stand for 120 seconds or less, then rinsing.

8. The method according to Claim 7, wherein the rinsing is carried out within 2 minutes from the application of the composition to the hair.

9. A hair dye composition substantially as herein described in the examples.

10. A method of using a hair dye composition as claimed in Claim 7 and substantially as herein described in the examples.

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